Mechanical Properties and Transition Temperatures for Copolymers of *N*-*n*-Alkylacrylamides and Acrylonitrile

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Synopsis

Random copolymers of *N*-*n*-butyl-, *N*-*n*-octyl-, or *N*-*n*-octadecylacrylamide with acrylonitrile were prepared in *tert*-butanol at 60°C. to test the effect of amide homologs as internal plasticizers. At room temperature under high deformations all samples showed brittle failure; at 100°C. flexible and resilient copolymers were obtained. At low deformations, torsional stiffness values T_f followed the equations of Wood, Fox, and Dimarzio and Gibbs, the latter two modified by use of mole fraction instead of weight fraction. Mole fraction appeared to function better than weight fraction for these special cases where $w_i > 2m_i$ and where modulus–temperature curves were broad. Because literature values for the glass (or brittle) temperatures of homologs of poly-*n*-alkyl acrylates, methacrylates, *n*-alkyl styrenes and alkenes, and estimated values for poly-*N*-*n*-alkylacrylamides, plotted as a function of the logarithm of the number of single bonds in repeat units, extrapolate to an average value of −111°C. at a chain length of eighteen carbon atoms, and because side-chain melting points of linear eighteen carbon side-chain homologs appear to have a common value of 48–50°C. regardless of structure, it was concluded that similar glass and melting transitions are obtained when the side chain reaches eighteen carbon atoms in any series of homologs. Transitions for longer side-chain lengths then approach the limit of a polyethylene graft, where T_g is −81°C. and T_m is 137°C.

INTRODUCTION

The introduction of a pendent group into the backbone chain of a polymer molecule profoundly affects its physical properties.[1] If the group is strongly polar, movement of the chain is restrained by intermolecular interaction. If the group is compactly bulky or the configuration allows intramolecular polar repulsions, the chain is internally stiffened. In contrast, if the pendent group is flexible or singly bonded, the backbone chain is rendered more flexible by reduced intermolecular interactions.

Polymer chain flexibility has been found by many investigators[1–8] to be particularly pronounced when the subgroup is a linear alkyl, the effect on homologs increasing proportionally as the side chain is lengthened. How-

ever, an apparent reversal of effect has often been observed when chain lengths are greater than about eight carbons,[2–6,8] which is attributed by some[5,9–11] to secondary crosslinks resulting from side-chain crystallinity. Similar behavior has been observed with copolymers. Copolymers possessing long, linear side chains were especially effective internal plasticizers, the effect again increasing as the side chains were lengthened, provided that the side chains were randomly distributed.[1,12–15] Efficiency[16] in these systems, while highest with amorphous comonomers,[1] was also high with comonomers whose homopolymers possessed moderate degrees of backbone crystallinity,[12,14] presumably because such crystallinity was largely eliminated.[17] Efficiency was lower in highly crystalline systems.[18]

Polyacrylonitrile consists of exceptionally stiff chains, yet possesses a low degree of crystallinity. Stiffness appears to result from large dipole and steric repulsions between neighboring cyano groups, which limit conformational modes and require considerable cooperation for motion between segments.[19] Interruption of stiff regions should result from random copolymerization with flexible comonomers. The *N*-alkylacrylamides should satisfy the requirement of randomness in copolymers because their reactivity ratios toward acrylonitrile were near unity.[20] While the requirement of flexibility is met by the singly bonded alkyl groups of the comonomers, intermolecular interactions caused by bonding through the unsubstituted hydrogen atom might lead to loss in conformational freedom. Thus, the high cohesive energy density of amides, while aiding solvation and plasticization of polyacrylonitrile in mechanical mixtures,[21] might, in copolymers, oppose high-deformation flexibility by introducing weak crosslinks.

To demonstrate the magnitude of these effects on properties, preliminary data are presented in this paper for some physical, thermal, and solution properties of copolymers of *N*-*n*-butyl-, *N*-*n*-octyl-, and *N*-*n*-octadecylacrylamides with acrylonitrile. Special attention is given to a characteristic low temperature (in this study the torsional stiffness temperature T_f), because of its importance in establishing plasticizer efficiency, as well as reflecting the presence of crystalline and polar crosslinks.[14] Means will be demonstrated for predicting T_f by using semiempirical equations originally proposed for predicting the glass temperature of copolymers. A general relationship is demonstrated between the characteristic temperature and the number of single bonds of homologs having linear side chains, which defines, to some extent, the limits of side-chain length and structure with respect to efficiency in lowering the characteristic temperature.

EXPERIMENTAL

Materials

Amines. The amines, the purest available commercially (99%), were used directly.

Acryloyl chloride. A commercial product, b.p. 75°C. at 760 mm., was used without purification.

***N*-*n*-Alkylacrylamides.** The three *N*-*n*-alkylacrylamides were prepared by acylation at 37°C. of the appropriate amine by the slow addition of acryloyl chloride (10 mole-% excess based on amine), with the use of triethylamine (10 mole-% excess based on amine) as the acid scavenger in anhydrous benzene (50 ml./g. of acryloyl chloride). Crude *N*-*n*-octadecylacrylamide was isolated by filtration after cooling the reaction flask to 10°C. It was treated with hot Skellysolve B (10 ml./g.), filtered to remove the amine salt, and cooled to 0°C. to isolate the amide, which was recrystallized once from acetone (10 ml./g.) at 0°C. Yields were 73.6%, m.p. (crystallized from the melt) 74.5–75.5°C., acid number 0.50.

ANAL. Calcd.: C, 77.95%; H, 12.77%; N, 4.33%. Found: C, 78.12%; H, 12.94%; N, 4.37%.

Crude *N*-*n*-octylacrylamide was freed of the amine salt by filtration at 10°C. After treatment of a benzene solution (5 ml./g.) of the amide with 10% HCl solution and water washes to remove all residual amine and salt, the dry amide was crystallized once from acetone, 10 ml./g. at −60°C. Yields were 84.0%, m.p. 34.5–35.5°C., acid number < 1.

ANAL. Calcd.: C, 72.15%; H, 11.47%; N, 7.65. Found: C, 72.19%, H, 11.49%; N, 7.48%.

Crude *N*-*n*-butylacrylamide was isolated by evaporation after salt removal and was flash distilled at 0.2 mm. To remove acidic substances, a benzene solution (5 ml./g.) was washed twice with a 50% excess of 10% sodium carbonate based on the free acid present and freed of alkali with a minimum of water (the amide was moderately soluble in water); the isolated amide was distilled through a Vigreux column at 88–92°C. at 0.01 mm. Hg. Yields were 50.2%. All amides were 99% pure by gas–liquid chromatography.

ANAL. Calcd.: C, 66.10%; H, 10.30%; N, 11.01%. Found: C, 66.53%; H, 10.47%; N, 11.05%.

Polymerization Procedure

Polymerizations were conducted in *tert*-butanol (4 mole/mole monomer. at 60°C. for 24 hr. with 0.2 mole-% of benzoyl peroxide as initiator). Dodecyl mercaptan (0.25 mole-% based on monomer) was used in compositions containing greater than 35 mole-% amide to prevent gelation. Inhibitor-free monomer, solvent, initiator, and regulator were charged into a flask which was cooled to −80°C., evacuated at 0.1 mm., and flushed repeatedly with nitrogen. No inhibition period was encountered when this treatment was used. Copolymers were isolated by pouring their *tert*-butanol suspensions into methanol (5 ml./g.) and extracting repeatedly with hot methanol till free of monomer. Copolymer composition was computed from analyses of per cent nitrogen.[21] To facilitate the use of

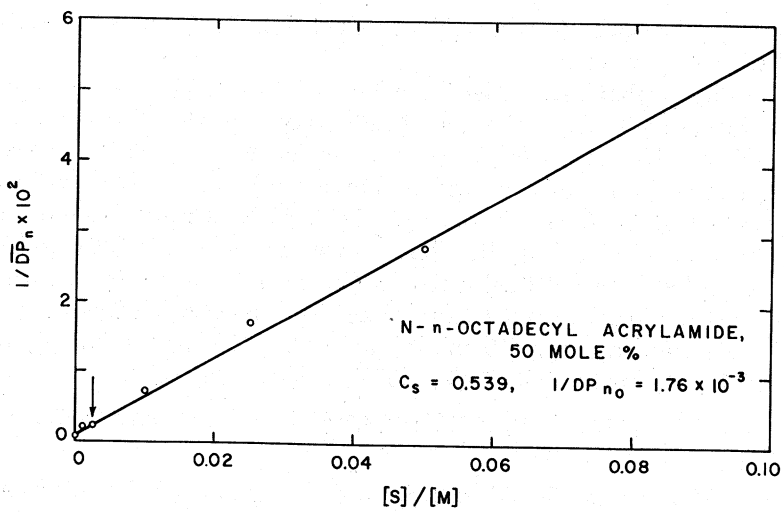

Fig. 1. Determination of the transfer constant for a 50–50 copolymer of dodecyl mercaptan in *tert*-butanol at 60°C.

dodecyl mercaptan to prevent gelation, while maintaining adequate molecular weights, transfer constants were determined from 50–50 comonomer compositions at 60°C., by using the polymerization recipe given above but varying the dodecyl mercaptan. The apparent transfer constant was calculated by the equation of Mayo:[22]

$$1/\overline{DP}_n = C_S[S]/[M] + 1/\overline{DP}_{n_0} \quad (1)$$

where [S]/[M] is the ratio of moles of dodecyl mercaptan to moles of total monomer, C_S, is the transfer constant; and $\overline{DP}_n$ is the degree of polymerization. The plot of the data together with the value of C_S and $1/\overline{DP}_{n_0}$ are illustrated in Figure 1. The arrow marks the concentration (0.25 mole-% based on total monomer) required to prevent gelation. The data indicate that this modification brought about a 40% reduction in molecular weight. Transfer to *tert*-butanol was considered negligibly small in comparison with that to the mercaptan.[23]

Solution Properties

Osmotic molecular weights were determined with a Mechrolab membrane osmometer, Model Number 501, and Schleicher and Schuell type 0–8 membranes. Duplicate determinations were made at 37°C. at four concentrations. Copolymers rich in acrylonitrile (5–15 mole-% octadecyl acrylamide and 5–35 mole-% octyl acrylamide and butylacrylamide) were run in dimethylformamide; the others were run with toluene as the solvent. Although relatively long equilibrium times (1 hr.) were required for each concentration in dimethylformamide, equilibrium times in toluene were 10 min. The instrument was checked on N.B.S. polystyrene #705 in sextuplicate with toluene as the solvent. The N.B.S. value was 172,000;

that of this laboratory was 177,000 ± 1.24%. The difference between the values was therefore 3%. A similar value was obtained with dimethylformamide as solvent.

Mechanical Properties

All samples were equilibrated at 23°C. and 50% R. H. for at least 24 hr. The tensile data were obtained with the use of an Instron tensile tester and the A.S.T.M. procedure for rigid materials, D638-61T. The flexural data were obtained with the Instron tensile tester by using a flexural testing accessory according to A.S.T.M. procedure D790-61. Flexural strength was measured at 5% strain, except when the sample broke at lower strain. Torsional stiffness temperatures were determined by the Clash-Berg method, A.S.T.M. standards designation D1043-61T.

Melting Temperature (T_m)

A Perkin-Elmer differential scanning calorimeter, DSC-1, Model No. 219, was run at speeds of either 5 or 10°C./min. with the use of sample weights of 7–8 mg. The calorimeter was calibrated by using the freezing points of indium and tin and the melting points of pure stearic acid and 9,10-dihydroxystearic acids.

Thermogravimetric Data

An Aminco Thermo-Grav, No. 4-4430, was used, and a Coors crucible No. 00000 was employed as the sample holder. All samples were run in dry air at a flow rate of 10 ml./min. at atmospheric pressure. The rate of temperature rise was 3°C./min.

Statistical Treatment

All data following linear relationships were statistically analyzed by regression analysis, and, where significant, the 95% confidence limits of the slope and intercept are given. In several cases (Tables IV and VI) a value of Y was computed for a specific value of X, and again the 95% confidence limits were computed.

RESULTS AND DISCUSSIONS

Mechanical, Thermal, and Solution Properties

In Table I are listed the compositions, melting points, and solution properties of the copolymers studied in this investigation. In general, the degrees of polymerization ($\overline{DP}_n$) indicated molecular weights high enough to confer mechanical properties typical of high polymers. The melting point of the side chains in polyoctadecylacrylamide, 48.3°C., as determined by differential scanning calorimetry, was very similar to those found by the same method for the side chains of both poly(vinyl stearate), 47.0°C., and poly(octadecyl acrylate), 48.5°C. This compares with a

TABLE I

Composition and Solution Properties of Copolymers of Acrylonitrile and *N*-*n*-Alkylacrylamides

Copolymer	Amide content: Monomer mix., mole-%	Amide content: Copolymer, Mole-%	Amide content: Copolymer, Wt.-%	Yield, %	M.p. of polymer side chains, °C.	Osomotic molecular weights: $\bar{M}_n$	Osomotic molecular weights: Deviation, %	Osomotic molecular weights: $\overline{DP}_n$
N-*n*-Butylacrylamide	0	0	0	87.3	No observable melting	58,900		1110
	5	7.33	16.04	87.4	"	55,000	3.82	969
	15	14.90	29.37	83.7	"	78,600	1.29	1225
	25	27.19	47.24	84.8	"	113,000		1578
	35	41.49	62.96	69.7	"	63,000	3.33	797
	50	62.73	80.05	69.2	"			
	75	80.53	90.84	77.8	"			
	100	100.00	100.00	86.6	"			
N-*n*-Octylacrylamide	5	5.88	17.75	89.5	No observable melting	51,300		861
	15	14.98	37.84	90.5	"	74,100		1021
	25	26.90	55.97	89.0	"	72,600	4.55	848
	35	37.47	67.43	75.2	"	76,900	4.10	779
	50	56.05	81.50	43.8	"			
	75	77.42	92.22	70.7	"	54,950	1.00	365
	100	100.00	100.00	57.1	"	87,800	4.50	479
N-*n*-Octadecylacrylamide	5	5.25	25.23	89.5	No melting	108,500	1.38	1630
	15	15.81	53.37	89.0	"	91,800	5.9	981
	25	26.22	68.42	91.6	44.5			
	35	37.23	78.34	83.1	51.0	123,200	0	834
	50	55.12	88.22	76.2	48.7	88,300	4.60	469
	75	80.37	96.15	82.6	51.0	105,750	0.52	413
	100	100.00	100.00	57.2	48.3	211,000	2.37	652

TABLE II. Mechanical and Thermogravimetric Properties of Copolymers of Acrylonitrile and *N*-*n*-Alkylacrylamides[a]

Acrylamide	Acrylamide in copolymer, mole-%	Tensile strength, psi	Tensile modulus, dyne/cm.^{2} × 10^{-10}	Flexural strength, psi	Flexural modulus, dyne/cm.^{2} × 10^{-10}	Thermogravimetric data	
						Onset of decomp., °C.	1% decomp., °C.
N-*n*-Butyl	0	3500[b]	2.28[b]	6,600[b]	2.07[b]		
	0	1200	1.36	4,800	1.90	237	237
	7.4	4500	2.14	5,700[c]	2.41	215	255
	14.9	9400	2.07	14,000	2.07	228	240
	27.2	8500	1.72	11,000	1.69	175	230
	41.5	8000	1.66	10,000	1.42	107	140
	62.7	5900	1.35	8,500	1.22		
	80.5	4700	1.21	6,600	0.95	110	205
	100.0	3000	0.83	4,700	0.69		
N-*n*-Octyl	5.9			8,100	1.64	247	260
	15.0	5300	1.45	8,700	1.17	234	250
	26.9	5600	1.13	6,000	0.80	252	265
	37.5	4600	0.89	4,500	0.61		
	56.1	3300	0.69	3,300	0.46	264	295
	77.4	2400	0.37	2,400[c]	0.28	175	215
	100.0	1900	0.23	1,300[c]	0.20	232	262
N-*n*-Octadecyl	5.3	5000	1.06	7,500[c]	1.08	259	259
	15.8	too brittle to test		5,400	0.61	255	277
	26.2	" " " "		3,000[c]	0.50	270	286
	37.2	" " " "		2,500[c]	0.48		
	55.1	" " " "		1,800[c]	0.40	245	307
	80.4	" " " "		1,000[c]	0.29	252	295
	100.0	" " " "		1,500[c]	0.24	188	241

[a] Samples 0.25 × 2.0 × 0.062 in. of copolymer without stabilizers or additives were molded for 3–5 min. at 200–450°C. at 20–30 tons; elongations were 3–10%; [b] Commercial sample; [c] Flexural strength at break.

capillary melting point for poly(octadecyl acrylate) of 50–51°C. and a refractometric melting point for poly(vinyl stearate) of 51.7°C.[11] Since the melting points of the amide, vinyl ester, and acrylic ester monomers were diverse, (74–75, 35–36, and 31–32°C.), it is possible that all polymers of this general structure with eighteen-carbon side chains melt at the same temperature. Diminished polar group contributions and correspondingly enhanced alkane contributions may account for this result. Peak heights of the copolymers became smaller as the amide content was reduced, vanishing entirely for the 15 mole-% copolymer, when the calorimeter was run under the same experimental conditions. Melting in the octyl and butyl systems was not found in the range −90 to 100°C., even though the melting point of *N*-*n*-octylacrylamide was 35°C. This agrees with previous observations concerning brittle behavior,[9,10] where a minimum in impact values was observed for an eight-carbon side chain.

The mechanical properties of the copolymers at 23°C. and 50% R.H. are listed in Table II. All of the samples tested exhibited brittle failure at ordinary temperature. Break strengths lower than yield strengths in both tension and flexure, accompanied by high moduli and low elongations, demonstrated the inability of these materials to withstand high deformations at reasonable loading times.[24] The effect was most pronounced with the octadecylacrylamide copolymers, in which brittleness was enhanced by the presence of the side-chain crystallites. Flexural and tensile moduli declined in going from the butylacrylamide to the octadecylacrylamide system, and, within each system, individual moduli also decreased with increase in amide content. Although lower moduli are in the direction of superior viscoelastic properties and therefore of lower yield strength, the latter property, while it may have declined, remained higher than the break strength for all the copolymers. Behavior of this kind has been predicted with some reservations for systems having side branches.[24] For similar degrees of polymerization, tensile and flexural strengths for the three systems declined as the amide side chain was lengthened. This reflects reductions in intermolecular cohesion with increasing volume requirements of the side chains.

At temperatures of about 100°C., however, thick films of the octylacrylamide and octadecylacrylamide copolymers were very tough and flexible, the flexibility increasing with chain length and amide content. At this temperature polyoctadecylacrylamide was a tacky, highly resilient material. The butyl series and samples of low amide content (<15 mole-%) remained brittle at 100°C. and broke easily. Thus, only when aided by moderate thermal agitation were flexible appendages to the polymer chains able to overcome the restraining effects brought about by the intermolecular interactions of this system.

Plots of flexural strength against the characteristic low temperature, T_f (discussed below) were linear, as has been found for many externally plasticized polymers,[25] and the slopes were in the proportion: octadecyl: octyl:butyl-1:1.6:6.7. This corresponds to the normal relation of flexural

strength to glass temperature, according to the principle of corresponding viscoelastic states[26a] as T_g is progressively lowered.

Thermogravimetric data, also listed in Table II, indicate that these copolymers have rather good higher temperature stabilities, this property decreasing, in general, in the order octadecyl > octyl > butyl. In most instances, the difference between the onset of decomposition, the temperature where the copolymers show a detectable weight loss, and 1% decomposition was small.

Characteristic Low Temperatures, T_f

Although at high deformations the copolymers studied exhibited poor mechanical properties, at low deformations their behavior resembled systems having randomly distributed, singly bonded side chains. This can be seen from the torsional stiffness temperatures listed in Table III. The torsional stiffness temperature T_f (at which Young's modulus reaches a value of 135,000 psi) lies between the glass temperature T_g and the inflection temperature T_i. Thus, for amorphous polymers T_f is only a few degrees higher than the glass temperature of most polymers.[26,27] As could be expected, the effect of reducing T_f, on a mole basis, decreased in the order octadecyl > octyl > butyl. Modulus–temperature curves were also found (T_4–T_f, Table III) to be very broad. In order to estimate by extrapolation the T_f temperature for the homopolymers of *N*-*n*-octylacrylamide and *N*-*n*-octadecylacrylamide, use was made of several equations which predict the glass temperature of a copolymer as some weighted average of the glass temperatures of the respective homopolymers.

All of the equations for the relation between glass temperature and copolymer composition, in terms of weight fraction w_i can be derived from a general equation, presented first by Wood.[28]

$$A_1w_1(T_g - T_{g1}) + A_2w_2(T_g - T_{g2}) = 0 \tag{2}$$

where T_{g1} and T_{g2} are the glass transition temperatures of two homopolymers, and A_1 and A_2 are constants. This may be rearranged to

$$T_g = A_2/A_1\,(T_{g2} - T_g)[w_2/(1 - w_2)] + T_{g1} \tag{3}$$

and

$$1/T_g = 1/[w_1 + (A_2T_{g2}/A_1T_{g1})w_2]\;[(w_1/T_{g1}) + (A_2T_{g2}/A_1T_{g1})(w_2/T_{g2})] \tag{4}$$

Equation (3) was first presented by Wood[28] and eq. (4) by Mendelkern and co-workers.[29] Simplifications can be made if certain relations exist among the constants. For example, if $A_2/A_1 = 1$, eq. (3) becomes

$$T_g = (T_{g2} - T_{g1})w_2 + T_{g1} \tag{5}$$

with a linear relation between T_g and w_2. If $A_2T_{g2}/A_1T_{g1} = 1$, eq. (4) becomes, according to Fox,[30]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{6}$$

TABLE III

Comparison of Observed and Calculated T_f Values Obtained in this Investigation[a]

Acrylamide	Amide in Copolymer, mole %	T_f, °K.				
		Observed	Calc. by equation of Wood[b]	Calc. by equation of Dimarzio and Gibbs[c]		Calc. by equation of Fox, using mole fraction[d]
				Using mole fraction	Using weight fraction	
N-*n*-Octadecylacrylamide	5.3	337	339	341	274	344
	15.8	310	303	304	204	307
	26.2	276	278	272	174	278
	37.2	268	257	242	157	252
	55.1	212	233	200	141	219
N-*n*-Octylacrylamide	5.9	350	351	351	331	356
	15.0	336	335	335	302	336
	26.9	326	317	317	281	313
	37.5	311	303	303	269	295
	56.1	257	283	280	235	268
N-*n*-Butylacrylamide	7.4	360	359	358	354	357
	14.9	356	355	355	349	353
	27.2	349	350	350	342	348
	41.5	338	344	344	337	343
	62.7	333	335	337	332	333
	80.5	328	329	332	329	326
	99.0	320	322	327	327	319

[a] Values of $T_4 - T_f$, increasing with amide content, covered these ranges: butyl 17–22°C.; octyl 24–58°C.; octadecyl 24–111°C; the octadecyl system showed side-chain crystallinity.

[b] Equation (3).

[c] Equations (16), (17).

[d] Equation (12).

with a linear relation between $1/T_g$ and w_2. The Fox equation can be put in a form convenient for plotting. Assigning symbols so that $T_{g2} > T_{g1}$, the equation is

$$1/T_g = [(1/T_{g1}) - (1/T_{g2})]w_1 + (1/T_{g2}) = Kw_1 + (1/T_{g2}) \quad (7)$$

with a linear relation between $1/T_g$ and w_1.

Wood[28] has shown that the general relation, eq. (2), can also be expressed in terms of mole fraction, m_1:

$$A_1M_1m_1(T_g - T_{g1}) + A_2M_2m_2(T_g - T_{g2}) = 0 \quad (8)$$

Special forms are:

$$T_g = (A_2M_2/A_1M_1)(T_{g2} - T_g)[m_2/(1 - m_2)] + T_{g1} \quad (9)$$

corresponding to eq. (3) and

$$1/T_g = 1/[m_1 + (A_2M_2T_{g2}/A_1M_1T_{g1})m_2] \times [(m_1/T_{g1}) + (m_2/T_{g2})] \quad (10)$$

corresponding to eq. (4). A simplified form, with a linear relation between T_g and m_2, corresponding to eq. (5), requires that $A_2M_2/A_1M_1 = 1$; a linear relation between $1/T$ and m_2, corresponding to eq. (6), requires that $A_2M_2T_{g2}/A_1M_1T_{g1} = 1$. The Fox equation in terms of mole fraction is then

$$1/T_g = (m_1/T_{g1}) + (m_2/T_{g2}) \quad (11)$$

Again this can be put in a form for plotting:

$$1/T_g = [(1/T_{g1}) - (1/T_{g2})]m_1 + (1/T_{g2}) = Km_1 + (1/T_{g2}) \quad (12)$$

where proportionality is to m_1.

From theoretical considerations different authors have given variants of the general relation that ascribe to the constants A_1 and A_2 a physical significance enabling one to calculate them from observations of other quantities. For example, Gordon and Taylor[31] give

$$A_i = \beta_{ir} - \beta_{ig} \quad (13)$$

where β_{ir} is the volume–temperature coefficient of the homopolymer in the rubber state and β_{ig} the coefficient in the glassy state. Mandelkern et al.[29] give

$$A_i = \beta_{ir} - k_w\beta_{ir} - \beta_i^* \quad (14)$$

where k_w is the fraction of free volume in the glassy state and is equal to about 0.025 and β_i^* is the volume–temperature coefficient of the occupied volume. Dimarzio and Gibbs[32] give

$$A_i = \alpha_i/M_i \quad (15)$$

TABLE IV

Parameters for Calculating T_f in Various Relationships

Equation	Amide	Parameter			95% confidence limits, $t_{05}s$		
		K	Intercept	T_{f1}, °K[a]	K	Intercept	$1/T_{f1}$
(12) Fox	Butyl	0.00371	0.00277	319	$\pm 0.49 \times 10^{-4}$	$\pm 0.27 \times 10^{-4}$	$\pm 0.58 \times 10^{-4}$
	Octyl	0.00184	0.00270	220	$\pm 2.39 \times 10^{-4}$	$\pm 2.29 \times 10^{-4}$	$\pm 6.04 \times 10^{-4}$
	Octadecyl	0.00333	0.00273	165	$\pm 8.22 \times 10^{-4}$	$\pm 2.47 \times 10^{-4}$	$\pm 7.53 \times 10^{-4}$
(3) Wood	Butyl	2.08	321.4	321.4	± 1.82	± 19.33	
	Octyl	1.97	246.9	246.9			
	Octadecyl	2.04	197.9	197.9	± 1.71	± 77.49	
(17) Dimarzio and Gibbs	Butyl			326.6			
	Octyl			240.2			
	Octadecyl			123.7			

[a] T_{f1} of 100% alkylacrylamide obtained by extrapolation, by using eqs. (3) or (12); the T_f for the 100% nitrile (T_{f2}) was experimentally observed to be 362°K. T_{f1} of the Dimarzio-Gibbs equation was the average of values obtained after insertion of each experimental point, T_f, into eq. (17).

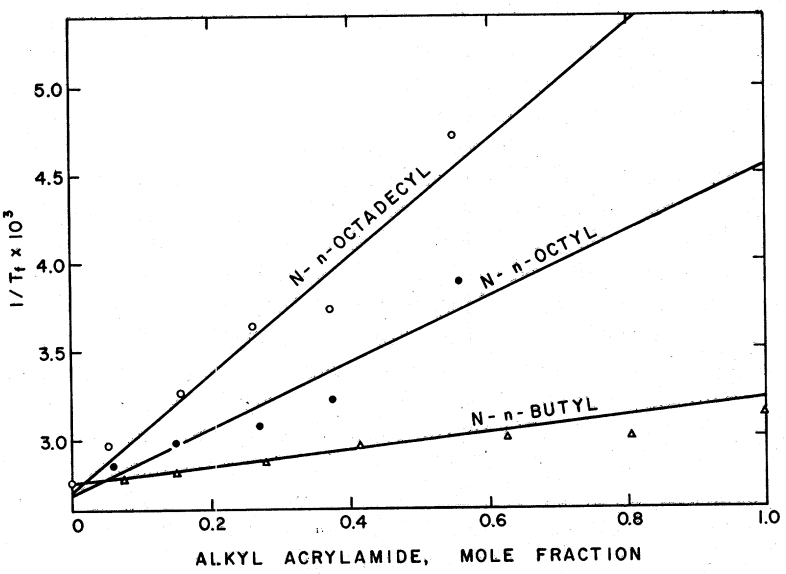

Fig. 2. Variation of the reciprocal T_f [eq. (12)] with the mole fraction of *N-n*-alkylacrylamide.

where α_i is the number of single bonds per monomer unit and M_i is the molecular weight of the monomer unit. Their equation is obtained by inserting eq. (15) into eq. (2) to give

$$T_g = w_1(\alpha_1/M_1)(T_g - T_{g1}) + w_2(\alpha_2/M_2)(T_g - T_{g2}) = 0 \qquad (16)$$

Various forms of eq. (2) were tested in this work as empirical relations for calculating torsional stiffness temperature T_f. Equations which estimated observed T_f values successfully were that of Wood [eq. (3)], one of Fox [eq. (12)], and the Dimarzio-Gibbs equation, with mole fraction m_i replacing weight fraction to give

$$T_f = m_1(\alpha_1/M_1)(T_f - T_{f1}) + m_2(\alpha_2/M_2)(T_f - T_{f2}) = 0 \qquad (17)$$

This is shown in Table III, where experimental values are compared with values calculated using the appropriate equation. The estimates of the parameters used for the calculations were obtained from regression analysis; they are reported together with T_f values computed for the *N-n*-alkylacrylamide homopolymer in Table IV. A plot is shown in Figure 2 of the experimental data for the three copolymer systems in the Fox relationship [eq. (12)].

The data in Table III show that all three relationships estimate the observed values fairly well with the exception of the form of the Dimarzio-Gibbs equation based on weight fraction. Because T_f occurs generally only a few degrees higher than T_g, it should be characterized by a very similar type of molecular motion. Perhaps this involves a small increase in the coordinated crankshaft motion of 30–40 segments often ascribed to

T_g.[33] It seemed reasonable, therefore, that the theoretical parameters for eqs. (13), (14), and (15) might also apply to T_f. An estimate of the ratio of the parameters, A_2/A_1, apart from their theoretical derivation, can be obtained by substituting experimental values of T_f in the Wood equation [eq. (3)]. Values found for A_2/A_1 (Table IV) were approximately 2. Substituting these in the Mandelkern equation for mole fraction [eq. (10)] should produce the parameter $A_2M_2T_{f2}/A_1M_1T_{f1}$, equal to unity. This reduces this equation to the Fox equation [eq. (12)], with proportionality of $1/T_f$ to m_1, as observed (Fig. 2). The values found for the Mandelkern parameter were: octadecylacrylamide, 0.734; octylacrylamide, 0.938; and butylacrylamide 0.985 (using Fox T_{f1}, Table IV). The low value for octadecylacrylamide may reflect experimental errors in some of the values making up the parameter in this case. Rearranging the modified Dimarzio Gibbs equation [eq. (17)] to the form of the Wood equation involving mole fraction [eq. (9)] is equivalent to multiplying the normal constant of the equation α_2/α_1 by M_1/M_2. Values found for α_2M_1/α_1M_2 were as follows: octadecylacrylamide, 0.581; octylacrylamide, 0.628; butylacrylamide, 0.685. Use of these constants in eq. (9) gave calculated results close to those observed.

The two equations using mole fraction [eqs. (12) and (17)] would seem to apply to cases where $w_i > 2 > m_i$ and where the molecule is stiffened by crosslinking caused by crystallinity or strong intermolecular bonding, producing broad modulus–temperature curves. Under these circumstances differences between T_g and T_f can become larger than the few degrees usually observed for amorphous sytems. It is possible that the regular forms of the equations predict T_g while T_f may be predicted as a trivial circumstance by mole fraction. Data of Tobolsky et al.[34] are shown in Table V for which T_g and T_f values were obtained and compared with computed values by using the Dimarzio-Gibbs equation for copolymers of 2-ethylhexyl acrylate and *n*-butyl acrylate with acrylonitrile. T_g was computed by using weight fraction in eq. (16) and T_f by using mole fraction in eq. (17). Agreement can be seen to be fairly good in both cases. Because of the chemical similarity of alkylacrylamide and alkyl acrylate copolymers with acrylonitrile, the reasons given seem to plausibly explain the behavior of both systems, particularly in view of the broad modulus-temperature curves observed. As additional evidence, copolymers of vinyl stearate and vinyl chloride,[12] for which modulus–temperature coefficients were much higher than in the present instance, follow more closely weight fraction relations [eq. (16)] than mole fraction [eq. (17)] in predicting T_f.

By plotting the value of K in the Fox relationship (Table IV) as a function of the number of carbon atoms in the side chain, the rate of change of K with respect to chain length was determined as the slope of the line. This is illustrated in Figure 3. Appropriate use of the regression coefficient, given in the figure, and the equation of Fox enables the calculation of T_f for any *N*-*n*-alkylacrylamide copolymer with acrylonitrile.

The weak mechanical behavior of these acrylamide copolymers, coupled

TABLE V

Comparison of Observed and Calculated T_g and T_f, Taken from Literature Data by Using Equation of Dimarzio and Gibbs.[a]

Ester in copolymer, mole-%	Copolymers of 2-ethylhexyl acrylate and acrylonitrile				Copolymers of *n*-butyl acrylate and acrylonitrile			
	T_g observed, °K.	T_g calcd. using wt. fraction, °K.	T_f observed, °K.[b]	T_f calcd. using mole fraction, °K.	T_g observed, °K.	T_g calcd. using wt. fraction, °K.	T_f observed, °K.[b]	T_f calcd. using mole fraction, °K.
0	352		362		352		362	
6.7	321	309	353	346				
10.0					317	321	351	342
13.2	313	281	343	331				
20.0	283	262	309	317	301	284	327	324
40.0	241	230	265	280	277	250	295	292
53.3	229	224	243	260				
60.0	214	219	233	250	249	230	265	265
69.8	213	208	227	237				
80.0	208	204	215	225	225	216	238	241
100.0	197		203		206		220	

[a] Data of Schaffhauser et al.[34]

[b] T_f estimated from modulus–temperature curves provided in the reference.

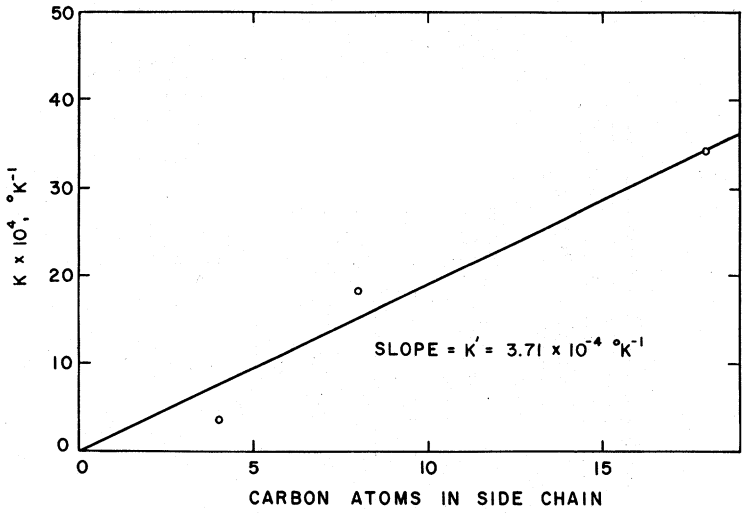

Fig. 3. Variation of the regression coefficient of the Fox equation with the number of carbon atoms in the side chain.

with their low modulus-temperature coefficients, and their T_f temperatures progressively lowered by increase in amide content, suggests behavior similar to that observed for certain graft copolymers, which are thought to exist in two phases.[35] The chains of such copolymers are mutually incompatible and retain their separate identity, even undergoing separate transitions. In the present system, on the basis of chemical composition, the side chains should be poor solvents for the backbone and should tend to aggregate. Aggregates of subgroups can separate chains and lower intermolecular interactions progressively as amide content increases, thus lowering torsional stiffness temperature and affecting mechanical properties in the manner observed. The segment-interrupting influence of homogeneous copolymerization should relieve the intramolecular dipole repulsions of the acrylonitrile and reduce stiffness. However, hydrogen bonding through cyano and amide groups can introduce intermolecular crosslinks and, by thus lowering chain mobility, give rise to the broad modulus–temperature curves observed. At high amide concentrations brittleness would be enhanced by a proliferation of aggregates of side chains acting as stress concentrators, the effect further intensified by side-chain crystallization. Although the data do not establish this system as existing in two discreet phases, this postulate can be used to explain the observed behavior.

The backbone chains of these copolymers may be mostly amorphous. The data of Howard[36] for copolymers of vinyl acetate and acrylonitrile showed that above 20 wt.-% of the acetate no crystallinity was present. In the present study, except for the 5 mole-% butyl and octyl copolymers, all of the amide compositions exceeded 20 wt.-%. The development of crystallinity, through increase in amide linkages, is not excluded however.

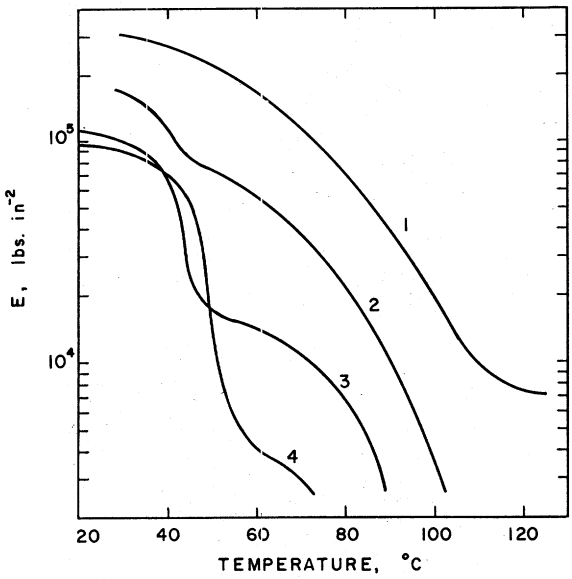

Fig. 4. Effect of side-chain crystallization on the shape of the curves of the modulus against temperature for selected copolymers of *N*-*n*-octadecylacrylamide and acrylonitrile. The numbers indicate amide composition: (*1*) 5 mole-%; (*2*) 15 mole-%; (*3*) 25 mole-%; (*4*) 50 mole-%.

Crystallinity appears to have only small effects on T_g, but T_f, measured by a test requiring higher deformation, could be more influenced. Isotactic polystyrene[37] containing 35% crystallinity, showed only a small (5–15°C.) rise in T_g over amorphous styrene of the same molecular weight, and the value depended on the method of test. Amorphous and semicrystalline forms of polychlorotrifluoroethylene showed no changes.[38]

No data showing effects on T_g (or T_f) for known proportions of side-chain crystallinity are available at the present time. However, the T_f data of this paper for the octadecylacrylamide copolymers, in which side-chain crystallinity was present, were in harmony with similar data for the octylacrylamide and butylacrylamide systems in which it was absent.

The effect of side-chain crystallinity on the slope of the Clash-Berg curves for *N*-*n*-octadecylacrylamide–acrylonitrile system is shown in Figure 4. The inflection occurs between 45 and 50°C., which is the range of T_m given in Table I, and its length is roughly proportional to amide content.

Relation between T_g and the Number of Flexible Bonds α in Homologs

The equations discussed earlier, especially the Dimarzio-Gibbs relation, illustrate that T_g is related to the number of single bonds in a subgroup system, since they have low energy requirements for rotation. The influence of the cumulative effects of these bonds on the characteristic low temperature T_c for the *N*-*n*-alkylacrylamide homologs was compared with

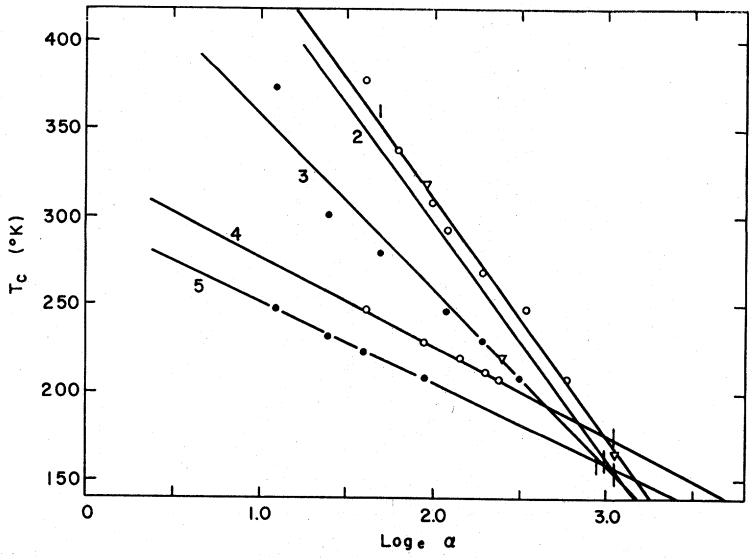

Fig. 5. Plots of characteristic low temperature T_c vs. the log of the number of single bonds, ln α: (*1*) *n*-alkyl methacrylates, T_g; (*2*) *N*-*n*-alkylacrylamides, T_f; (*3*) *n*-alkyl acrylates, T_b; (*4*) *n*-alkylstyrenes, T_g; (*5*) *n*-alkenes, T_g.

similar data for long-chain homologs of different chemical structures. When literature values of T_g (or brittle temperature T_b) for homologs of the *n*-alkyl acrylates,[2] methacrylates,[2,5] styrenes,[6] alkenes,[7] and *N*-*n*-alkylacrylamides (Table IV) were plotted as a function of the number of flexible bonds α, the relationship found was nonlinear. However, plots of T_g (or T_b) as a function of ln α were linear, as had been noted previously for two systems.[2] It therefore follows that

$$-dT_g/d\alpha = k/\alpha \tag{18}$$

and

$$T_g = -k \ln \alpha + T_{g0} \tag{19}$$

where T_g is the glass temperature for a given homolog and $-k$ and T_{g0} are the slope and intercept, respectively. Estimates of the parameters, obtained from regression analysis (together with their 95% confidence limits) for the literature homologs mentioned above, and for the *N*-alkylacrylamide homologs, are listed in Table VI. It seems from eq. (19) that the effectiveness of individual bonds in reducing T_g falls off logarithmically with distance from the main chain.

Characteristic temperatures computed for the case where each homolog had an eighteen carbon side chain are listed in column 6 of Table VI. All the values are reasonably similar. Selected data from the literature[2,5–7] and this work were plotted by using eq. (19) and are illustrated in Figure 5, where the values at C_{18} are marked by vertical lines. The data in the table and

TABLE VI

Parameters Relating the Characteristic Temperature to the Number of Flexible, Straight-Chain Bonds

Homopolymer system	Reference	Type of measurement	$-k$, °K.	T_{c0}, °K.[a]	T_c at C_{18}, °K.[b]	95% Confidence limits, $t_{05}s$		
						$-k$, °K.	T_{c0}, °K.	T_c at C_{18}, °K.
n-Alkyl acrylates	2	T_b	50.96	328.7	173.5	± 7.89	± 16.6	± 9.3
n-Alkyl methacrylates	2	T_b	85.38	469.8	205.9	± 21.58	± 49.5	± 53.2
n-Alkyl methacrylates	5	T_g[c]	136.7	584.9	162.4	± 22.61	± 49.1	± 32.2
n-Alkylstyrenes	6	T_g[c]	106.8	471.6	151.6	± 26.40	± 52.7	± 46.2
n-Alkenes	7	T_g[c]	46.98	298.9	160.6	± 4.36	± 6.7	± 6.1
N-*n*-Alkylacrylamides[d]	This work	T_f	184.4	684.3	122.9	± 38.50	± 96.4	± 41.4
N-*n*-Alkylacrylamides[e]	This work	T_f	136.4	570.6	155.3			

[a] T_c = characteristic temperature; T_{c0} is the intercept.

[b] Calculated values.

[c] Average value T_g = 161.7°K.

[d] T_{f1} from Dimarzio and Gibbs equation, Table IV.

[e] Using T_{f1} of Fox equation, Table IV.

in the plot show that many different structures acquire about the same T_g (or T_b) when the alkyl chain reaches eighteen carbon atoms. A tentative conclusion may therefore be drawn that most structures containing eighteen carbon atoms arranged in a linear side chain will have a characteristic low temperature near the computed mean of −111°C., given in Table VI. Of course, this extrapolation is too insensitive to distinguish between T_g and T_b. The apparently constant melting point also found for eighteen-carbon polyacrylamides, acrylate esters, and vinyl esters supports this conclusion. It is pertinent that Rogers and Mandelkern[5] estimated the value of T_g for poly(octadecyl methacrylate) to be −100°C., by extrapolation from linear plots of T_g versus specific volumes for homologs at 120°C. The value of −111°C., when used as T_{f1} in eqs. (11) and (17), produced values almost as close to observed values as were the corresponding values given in Table III.

A second tentative conclusion is that the relation of eq. (19) would not hold much further than to the neighborhood of this chain length. For example, at a chain length of C_{27} for an alkyl methacrylate, the computed T_g is −153°C., about as low as the lowest values found for the neat external plasticizers. This seems too low a transition to be reasonable for a copolymer. Grieveson[39] has shown that values of T_g for the homologs discussed in this paper, plotted as a function of increasing mole fraction of ethylene as the side-chain length was increased, reached on extrapolation a limit value of −165°C., which he considered to be the T_g of polymethylene. It would seem that the limiting case would be a side chain of linear polyethylene. Because amorphous polyethylene has a T_g of about −81°C.,[26b] a relationship whereby T_g approaches this limit value asymptotically seems indicated and has been suggested.[8] The higher T_m of polyethylene (137°C.)[1] over the eighteen-carbon homologs (48°C.) suggests a corresponding rise in T_g for the polymeric chain because of the known parallel relation between T_m and T_g.[1] Thus for symmetrical polymers

$$T_g/T_m = 0.5 \tag{20}$$

This ratio for the C_{18} homologs (162/321°K.) is 0.50; for polyethylene (192/410) the ratio is 0.48. With respect to transition temperatures the C_{18} homologs behave like grafted oligomers of polyethylene and appear to be relatively insensitive to chemical structure.

The authors express their appreciation to Mr. Joe N. Boyd and Miss Mirita J. Smithey of the Biometrical Services group of this laboratory for the regression analyses and determinations of variance. The authors also wish to express their thanks to Mr. David R. Grudem, Mr. Marvin J. Rudolph, and to Mr. John Pensabene for their assistance in the preparation of monomers and copolymers. Special thanks is extended to one of the reviewers for a helpful exposition of the interrelations of the various equations.

Reference to individual companies does not imply endorsement by the department over others not mentioned.

References

1. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, pp. 11–30.
2. C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).
3. R. H. Wiley and G. M. Brauer, *J. Polymer Sci.*, **3**, 647 (1948).
4. F. A. Bovey, J. F. Abere, G. B. Rathmann, and C. L. Sandberg, *J. Polymer Sci.*, **15**, 520 (1955).
5. S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
6. C. G. Overberger, C. Frazier, J. Mandelmann, and H. F. Smith, *J. Am. Chem. Soc.*, **75**, 3326 (1953).
7. M. L. Dannis, *J. Appl. Polymer Sci.*, **1**, 121 (1959).
8. G. Natta, F. Danusso, and G. Moraglio, *J. Polymer Sci.*, **25**, 119 (1957).
9. S. A. Greenberg and T. Alfrey, *J. Am. Chem. Soc.*, **76**, 6280 (1954).
10. H. S. Kaufman, A. Sacher, T. Alfrey, and I. Fankuchen, *J. Am. Chem. Soc.*, **70**, 3147 (1948).
11. W. S. Port, J. E. Hansen, E. F. Jordan, Jr., T. J. Dietz, and D. Swern, *J. Polymer Sci.*, **7**, 207 (1951).
12. W. S. Port, E. F. Jordan, Jr., W. E. Palm, L. P. Witnauer, J. E. Hansen, and D. Swern, *Ind. Eng. Chem.*, **47**, 472 (1955).
13. W. S. Port, E. F. Jordan, Jr., J. E. Hansen, and D. Swern, *J. Polymer Sci.*, **9**, 493 (1952).
14. E. F. Jordan, Jr., W. E. Palm, L. P. Witnauer, W. S. Port, *Ind. Eng. Chem.*, **49**, 1695 (1957).
15. E. F. Jordan, Jr., W. E. Palm, W. S. Port, *J. Am. Oil Chemists' Soc.*, **38**, 231 (1961).
16. I. Mellan, *The Behavior of Plasticizers*, Pergamon Press, New York, 1961, pp. 69–74.
17. F. W. Billmeyer, Jr., *Textbook of Polymer Science*, Interscience, New York, 1962, pp. 218–219.
18. E. F. Jordan, Jr., W. E. Palm, D. Swern, L. P. Witnauer, and W. S. Port, *J. Polymer Sci.*, **32**, 33 (1958).
19. W. R. Krigbaum and N. Tokita, *J. Polymer Sci.*, **43**, 467 (1960).
20. E. F. Jordan, Jr. and A. N. Wrigley, *J. Appl. Polymer Sci.*, **8**, 527 (1964).
21. E. E. Walker, *J. Appl. Chem. (London)*, **2**, (1952).
22. F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943).
23. S. K. Das, S. R. Chatterjee, and S. R. Palit, *Proc. Roy. Soc. (London)*, **A227**, 252 (1955).
24. P. I. Vincent, *Polymer*, **1**, 425 (1960).
25. R. F. Boyer, *J. Appl. Phys.*, **22**, 723 (1951).
26. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960, (a) pp. 60–83; (b) p. 321.
27. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, pp. 216–218.
28. L. A. Wood, *J. Polymer Sci.*, **28**, 319 (1958).
29. L. Mandelkern, G. M. Martin, and F. A. Quinn, Jr., *J. Res. Natl. Bur. Stds.*, **58**, 137 (1957).
30. T. G Fox, *Bull. Am. Phys. Soc.*, [2] **1**, 123 (1956).
31. M. Gordon and J. S. Taylor, *J. Appl. Chem. (London)*, **2**, 493 (1952).
32. E. A. Dimarzio, and J. H. Gibbs, *J. Polymer Sci.*, **40**, 121 (1959).
33. R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).
34. R. Schaffhauser, A. Evnin, and A. V. Tobolsky, U.S. Dept. Comm. Office Tech. Serv., AD 289,399, 9 pp (1962); ONR Rept. RLT-52.
35. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, pp. 172–177.
36. W. H. Howard, *J. Appl. Pol. Sci.*, **5**, 202 (1961).

37. S. Newman and W. P. Cox, *J. Polymer Sci.*, **46**, 29 (1960).
38. J. D. Hoffman and J. J. Weeks, *J. Res. Natl. Bur. Stds.*, **60**, 465 (1958).
39. B. M. Grieveson, *Polymer*, **1**, 499 (1960).

Résumé

Les copolymères statistiques de *N*-*n*-butyl, *N*-*n*-octyl et *N*-*n*-octadécylacrylamide avec l'acrylonitrile ont été préparés dans le *t*-butanol à 60°C en vue d'examiner l'effet des homogues amides comme plastifiant interne. À température de chambre, sous déformation élevée, tous les échantillons montraient une cassure fragile; à 100°C des copolymères flexibles et résiliants étaient obtenus. A basse déformation les valeurs de la rigidité à la torsion T_f suivaient des équations de Wood, Fox et Dimarzio et Gibbs, ces derniers étant modifiés par l'utilisation de la fraction molaire au lieu de la fraction en poids. La fraction molaire semblait être mieux utilisable que la fraction pondérale pour les cas spéciaux où w_i est plus grand que $2m_i$ et où les courbes module–température étaient larges. Vu les données de la littérature pour les températures de transition vitreuse des homologues des polyacrylates, polyméthacrylates de poly-*n*-alcoyle, et poly-*n*-alcoyl-styrène et polyalcènes, et les valeurs estimées pour le poly-*N*-*n*-alcoylacrylamides, et vu que ces valeurs portées en diagramme en fonction du logarithme du nombre de liens dans l'unité périodique donnaient par extrapolation une valeur moyenne de -111°C pour une longueur de chaînes de 18 atomes de carbone, et vu que les points de fusion des homologues à chaîne latérale à 18 atomes de carbone semblent avoir une valeur commune de 48 à 50°C indépendamment de leur structure, on a conclu que des transitions vitreuses et points de fusion similaires étaient toujours obtenus lorsque la chaîne latérale atteint 18 atomes de carbone pour n'importe quelle série homologue. Les transtions pour des longueurs de chaînes latérales encore plus grande, s'approche de la limite du polyéthylène greffé lorsque T_g est égal à -81°C et T_m est égal à 137°C.

Zusammenfussung

Statistische Copolymere aus *N*-*n*-Butyl-, *N*-*n*-Octyl- oder *N*-*n*-octadecylacrylamid und Acrylnitril wurden zur Testung der Wirkung der Amidhomologen als innere Weichmacher in *t*-Butanol bei 60°C hergestellt. Bei Raumtemperatur zeigten alle Proben bei hoher Verformung spröden Bruch; bei 100°C konnten biegsame und elastische Copolymere erhalten werden. Bei geringer Deformation befolgten die Werte für die Torsionssteifigkeit T_f die Gleichungen von Wood, Fox und Dimarzio und Gibbs, wobei die letzteren beiden durch Einführung der Molenbrüche an Stelle der Gewichtsbrüche modifiziert wurden. Molenbrüche schienen in diesen speziellen Fällen, in welchen $w_i > 2m_i$ und die Modul–Temperaturkurven breit waren, besser geeignet zu sein als Gewichtsbrüche. Da Literaturwerte für die Glas(oder Sprödigkeits-)-temperatur von homologen Poly-*n*-alkylacrylaten, -methacrylaten, *n*-alkylstyrolen und -alkenen sowie die für Poly-*N*-*n*-alkylacrylamiden bestimmten Werte beim Auftragen als Funktion des Logarithmus der Anzahl der Einfachbindungen in den Kettenbausteinen sich auf einen mittleren Wert von -111°C bei einer Kettenlänge von achtzehn Kohlenstoffatomen extrapolieren lassen und da Seitenkettenschmelzpunkte von Homologen mit linearen Seitenketten mit achtzehn Kohlenstoffatomen ohne Rücksicht auf fie Struktur einen gemeinsamen Wert von 48–50°C zu besitzen scheinen, wurde geschlossen, dass bei Erreichung von achtzehn Kohlenstoffatomen in der Seitenkette in allen homologen Reihen ähnliche Glas- und Schmelzumwandlungen erhalten werden. Umwandlungen für grössere Seitenkettenlängen nähern sich dann dem Grenzwert einer Polyäthylenaufpfropfung, für welche T_g gleich -81°C und T_m gleich 137°C ist.